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3,5-DIKETOPYRAZOLIDINE DERIVATIVES. I.

By Tokuichi TSUMAKI.

Received November 22, 1930. Published January 28, 1931.

When we try to obtain the acyl-derivatives of hydrazobenzene by substituting the hydrogen atoms attaching to the imino-groups in hydrazobenzene by acyl-groups, we sometimes obtain, as the results of the reaction, the derivatives of benzidine instead of those of hydrazobenzene. The difficulty to obtain the acyl-derivatives of the latter compound lies in the fact that the hydrazobenzene frequently undergoes benzidine transformation by various reagents.

D. Stern[1] carried out the reaction between hydrazobenzene and benzoyl chloride, and obtained contrary to his expectation dibenzoylbenzidine as a reaction product. In the case of the reaction between formic acid and hydrazobenzene, the analogous result was brought about, producing diformylbenzidine.

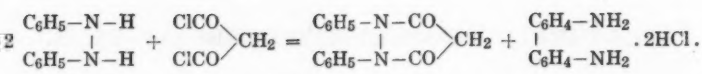
But several acyl-derivatives of hydrazobenzene are also obtained under suitable condition. For example, D. Stern obtained monoacetyl-hydrazobenzene under the action of acetic anhydride on hydrazobenzene, and also diacetyl-hydrazobenzene by heating the above two substances for a long time. C. A. Bischoff[2] obtained various bromoacyl-compounds from α-bromofatty acids and hydrazobenzene. J. Biehringer and A. Busch[3] produced monobenzoylhydrazobenzene by the action of benzoyl chloride on hydrazobenzene in alcohol in presence of slaked lime. H. P. Kaufmann[4] prepared acylated hydrazobenzenes by the action of succinyl chloride and *o*-phthalyl chloride respectively on hydrazobenzene in dimethylaniline.

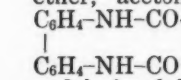
The author carried out the reaction between malonyl chloride and hydrazobenzene in the ether solution under cooling, and was able to isolate the colourless crystals, melt at 178°, by extracting the white precipitate, instantly produced in the ether solution, with petroleum ether.

On close inspection, this substance was proved to be a heterocyclic compound, namely, 1,2-diphenyl-3,5-diketopyrazolidine produced by substituting the hydrogen atoms of imino-groups in hydrazobenzene according to the following equation. Benzidine hydrochloride was simultaneously formed.

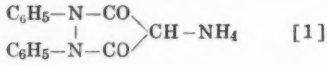
---

(1) Stern, *Ber.*, **17** (1884), 379.
(2) Bischoff, *Ber.*, **31** (1898), 3241.
(3) Biehringer and Busch, *Ber.*, **36** (1903), 137.
(4) Kaufmann, *Z. angew. Chem.*, **40** (1927), 69.

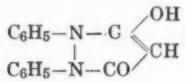


This compound forms colourless crystals and is soluble in alcohol, ether, acetone, chloroform and hot ligroin, while malonylbenzidine,  , prepared by Remfry[1] in 1911 has bluish gray colour, and is insoluble in almost all the ordinary organic solvents. The former bears some resemblance in its chemical properties to the derivatives of pyrazolone and pyrazolidone, especially to 1-phenyl-3,5-diketopyrazolidine described by Michaelis.[2]

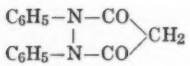
It is insoluble in water, but soluble in alkali solution forming its salt. For example, the ammonium salt [1] is easily obtained as the colourless crystals, when the strong ammoniacal solution of diphenyl-diketopyrazolidine is evaporated up to dryness. M.p.: 138°–139°.



The constitution of diphenyl-diketopyrazolidine may be expressed as the enolic form [2], or the ketonic form [3], and the formation of salts may approve of the former formula.



[2]



[3]

But, the easiness with which diphenyl-diketopyrazolidine condenses with aldehydes, ketones and nitrous acid, as stated in the following, shows us the existence of a methylene group in this compound, the author, therefore, prefers the formula [3], and has expressed its ammonium salt as diketo-compound as above.

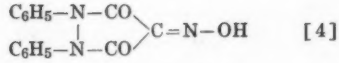
Diphenyl-diketopyrazolidine is fairly stable, and is not decomposed by dilute acid nor by alkali. From its alkali solution, it is reprecipitated as white crystals unaltered, after neutralizing the solution with acid. It seems to be decomposed by heating with conc. alcoholic potash solution, but neither hydrazobenzene nor benzidine can be detected in the decomposition product, which shows that the compound is not simply hydrolysed into its components.

---

(1) Remfry, *J. Chem. Soc.*, **99** (1911), 621.

(2) Michaelis and Burmeister, *Ber.*, **25** (1892), 1502.

By the action of nascent nitrous acid, diphenyl-diketopyrazolidine forms isonitroso-compound; namely, 1,2-diphenyl-4-isonitroso-3,5-diketopyrazolidine [4].

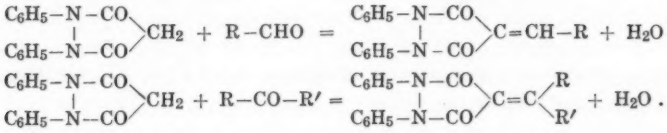


[4]

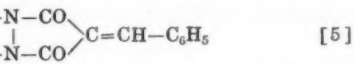
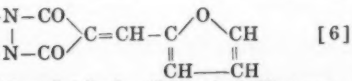
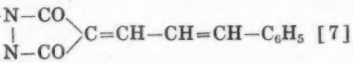
This compound contains two molecules of water of crystallization, and crystallizes in orange-red needles, while the anhydride forms dark red crystals and melts at 163°–164°.

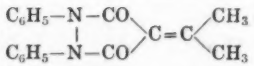
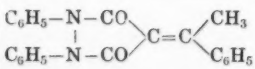
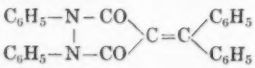
Diphenyl-diketopyrazolidine condenses with aldehydes and ketones forming various coloured substances. Its condensation with aldehydes is accomplished especially smoothly, and the products are obtained with good yields, only by heating the two components together on the water-bath for a short time; while its condensation with ketones requires more time and higher temperature.

At any late, the reactions with aldehydes and ketones are expressed by the following general formulae:—



The condensation products synthesised by the author are as follows.

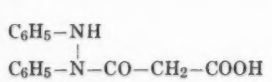
Aldehyde or ketone.	Condensation product.	M.p., °C.	Colour.
Benzaldehyde.	 [5] 1, 2-Diphenyl-4-benzylidene-3, 5-diketopyrazolidine.	164–165	Orange red.
Furfurol.	 [6] 1, 2-Diphenyl-4-furfurylidene-3, 5-diketopyrazolidine.	157–158	Dark red.
Cinnamaldehyde.	 [7] 1, 2-Diphenyl-4-cinnamylidene-3, 5-diketopyrazolidine.	190–192	Violet-tinged red.

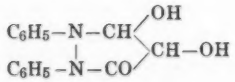
Aldehyde or ketone.	Condensation product.	M.p., °C.	Colour.
Acetone.	 [8] 1, 2-Diphenyl-4-isopropylidene-3, 5-diketopyrazolidine.	113	Canary yellow.
Acetophenone.	 [9] 1, 2-Diphenyl-4-[α-phenylethylidene]-3, 5-diketopyrazolidine.	148–149	Yellow.
Benzophenone.	 [10] 1, 2-Diphenyl-4-[diphenylmethylene]-3, 5-diketopyrazolidine.	269	Reddish yellow.

These products are easily decomposed by hot alkali solution, reproducing aldehydes or ketones.

In addition to diphenyl-diketopyrazolidine, another substance of colourless needles was obtained from the ethereal part of the product of the above-mentioned reaction between malonyl chloride and hydrazobenzene. It dissolves in caustic soda solution, and is reprecipitated by the addition of acid. It is soluble in ordinary organic solvents, but insoluble in ligroin, and its constituent corresponds to the formula $C_{15}H_{14}O_3N_2$. M.p.: 160°–162°.

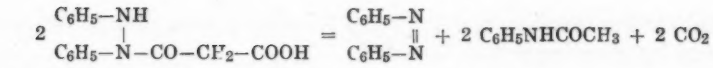
From its mode of formation, the constitution of this compound may be conjectured to be [11] or [12].


[11]

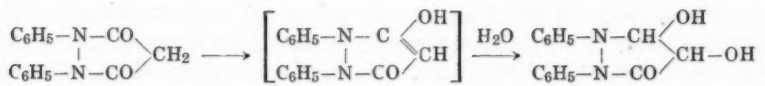

[12]

And if the former is true, it is expected that the compound will undergo the following decomposition on heating, forming azobenzene, acetanilide and carbon dioxide, in the same manner observed by Melms and others[1] on hydrazobenzene, or by Stern[2] on monoacetyl-hydrazobenzene.

(1) Melms, *Ber.*, **3** (1870), 554; Lermontow, *Ber.*, **5** (1872), 235.
(2) Stern, *Ber.*, **17** (1884), 379.



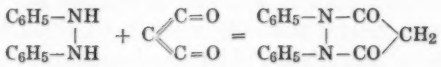
But in reality, nothing of these decomposition products could be detected. It is, therefore, presumed that the compound is [12], namely, the derivative of pyrazolidone, which undergoes complex decomposition under the influence of heat. Moreover, the same compound was produced when diphenyl-diketopyrazolidine, dissolved in the mixed solution of chloroform and alcohol, was allowed to stand for a few days after adding a few drops of dilute hydrochloric acid. In this case, diphenyl-diketopyrazolidine must be hydrated by the catalytic action of acid as in the following,



[3] [12]

On the other hand, the formation of [11] from diphenyl-diketopyrazolidine by hydrolysis with dilute hydrochloric acid is thought to be unprobable, as it is not hydrolysed into hydrazobenzene, as mentioned above, even with concentrated acid. In view of these facts, the compound in question is considered as [12], namely, 1, 2-diphenyl-3, 4-dihydroxy-5-pyrazolidone. It does not form isonitroso-compound with nitrous acid, as it has no methylene group in the molecule.

Parallel to the reaction between malonyl chloride and hydrazobenzene, the author carried out the reaction between carbon suboxide and hydrazobenzene, expecting that the reaction must be a suitable method for the preparation of diphenyl-diketopyrazolidine, as there is in this case no fear of benzidine transformation.



[3]

In fact, the same substances as were obtained by the action of malonyl chloride on hydrazobenzene, were also obtained in this case. But, the yields of them were very poor owing to the polymerization of the greater part of carbon suboxide into brownish black substance during the reaction.

Experimental Part.

A. The Reaction between Malonyl Chloride and Hydrazobenzene. *1,2-Diphenyl-3, 5-diketopyrazolidine*, [3]. Malonyl chloride, used as a

material for the reaction, was prepared principally according to the method described by Staudinger and Bereza.[1]

Fifty grams of powdered malonic acid and 160 gr. of thionyl chloride were heated in a flask under a reflux condenser for 60 hours at 40°, and then for 8 hours at 50°. The crystals of malonic acid went into solution forming the brownish liquid. It was then distilled under diminished pressure, and the fraction which boiled at 60° under 30 mm. pressure was collected as malonyl chloride.

A solution of 18.5 gr. of hydrazobenzene in 300 c.c. of ether was dropped from the tap-funnel into 200 c.c. of ether containing 10 gr. of malonyl chloride, and the white precipitate instantly produced in the flask was quickly filtered and well washed with ether, without exposing to moist air, as otherwise, the precipitate would change into a non-filterable viscous matter of brownish black colour. Diphenyl-diketopyrazolidine was obtained by extracting this precipitate with petroleum ether, and was recrystallized from ethyl alcohol. The yield was 6 gr. It crystallizes in colourless plates melting at 178°. It is insoluble in water and cold petroleum ether, but prettily soluble in alcohol and ether, and very soluble in acetone and chloroform. It dissolves in ammonia or in alkali solution, forming its salt.

Anal. Subst.=0.1095; CO_2=0.2862; H_2O=0.0490 gr. Found: C=71.28; H=5.01%. Calc. for $C_{15}H_{12}N_2O_2$: C=71.41; H=4.80%.

Subst.=0.1850 gr.; N_2=17.8 c.c. (12°, 763 mm.) Found: N=11.50%. Calc. for $C_{15}H_{12}N_2O_2$: N=11.11%.

1, 2-Diphenyl-3, 4-dihydroxy-5-pyrazolidone, [12]. The ethereal filtrate, obtained by filtering the above-mentioned precipitate by the reaction between malonyl chloride and hydrazobenzene, was washed with water to decompose the excess of malonyl chloride remained in the solution. It was then shaken with an one percent solution of sodium carbonate. The soda solution gave a light yellow precipitate when acidified with hydrochloric acid. The precipitate was dissolved in the least quantity of chloroform, and alcohol was added to it, and the solution was allowed to stand for one day. From this solution, 1,2-diphenyl-3,4-dihydroxy-5-pyrazolidone crystallized in colourless needles. It melts at 160°–162°. Before melting it seems to be somewhat decomposed. It is soluble in ether and chloroform, sparingly soluble in alcohol, ligroin and water.

Anal. Subst.=0.1204; CO_2=0.2956; H_2O=0.0550 gr. Found: C=66.94; H=5.08% Calc. for $C_{15}H_{14}O_3N_2$: C=66.67; H=5.18%.

Subst.=0.1454 gr.; N_2=12.8 c.c. (13°, 761 mm.) Found: N=10.45%. Calc. for $C_{15}H_{14}O_3N_2$: N=10.37%.

(1) Staudinger and St. Bereza, *Ber.*, **41** (1908), 4463.

The same compound was obtained from 1, 2-diphenyl-3, 5-diketopyrazolidine by dissolving the latter in the mixed solution of chloroform and alcohol, and allowing it to stand for a few days after the addition of a small quantity of dilute hydrochloric acid.

B. The Reaction between Carbon Suboxide and Hydrazobenzene. According to the method of Staudinger and Bereza,[1] dibromomalonic acid was treated with phosphorus pentachloride in ether, and the liquid which boiled at 74°–75° under 17 mm. pressure was collected as dibromomalonyl chloride; and was used as a material for the preparation of carbon suboxide.

To the flask containing 30 gr. of zinc granules, 450 c.c. of ether solution containing 45 gr. of dibromomalonyl chloride was added from the tap-funnel, and the evolved carbon suboxide gas and the vapour of ether were introduced to a condenser which was connected to another flask containing the ethereal solution of 20 gr. of hydrazobenzene and cooled with freezing mixture. A small amount of white precipitate was produced in the ethereal solution. 1,2-Diphenyl-3,5-diketopyrazolidine was obtained from this precipitate when recrystallized from petroleum ether. Hydrogen chloride gas was then passed through the ethereal solution in order to precipitate the excess of hydrazobenzene as benzidine hydrochloride. The ethereal solution was washed with water, and evaporated up to dryness, and the reddish brown residue was washed with petroleum ether to remove azobenzene included in it. A small amount of colourless needles was obtained from this brownish residue when recrystallized from alcohol, and this compound was proved to be identical with diphenyl-dihydroxypyrazolidone obtained from malonyl chloride and hydrazobenzene.

C. The Derivatives of 1,2-Diphenyl-3,5-diketopyrazolidine. *Ammonium salt of 1, 2-diphenyl-3, 5-diketopyrazolidine*, [1]. When the ammonical solution of diphenyl-diketopyrazolidine was allowed to stand in a vacuum desiccator furnished with soda lime till the solution was evaporated to dryness, the ammonium salt was remained as the colourless crystals. M.p.: 138°–139°.

Anal. Subst.=0.1262 gr.; N_2=17.1 c.c. (18.5°, 762 mm.) Found: N=15.70%. Calc. for $C_{15}H_{15}O_2N_3$: N=15.61%.

1,2-Diphenyl-4-isonitroso-3,5-diketopyrazolidine, [4]. To the caustic potash solution of 2 gr. of diphenyl-diketopyrazolidine, 0.6 gr. of sodium nitrite was added, and the excess of dilute hydrochloric acid was dropped

(1) Staudinger and St. Bereza, *Ber.*, **41** (1908), 4461.

to this solution under cooling. Isonitroso-compound was deposited out at once as a yellow precipitate, which gave the long needle crystals of orange colour on recrystallization from hot water. The yield was 0.5 gr. It contains two molecules of water of crystallization, and the anhydrous compound has dark red colour and melts at 163°–164°. It is soluble in alcohol, benzene, ether and hot water, but insoluble in ligroin.

Anal. Subst.=0.0253; lost at 100°=0.0029 gr. Found: H_2O=11.5%. Calc. for $C_{15}H_{11}O_3N_3 \cdot 2H_2O$: H_2O=11.4%.

Subst.=0.1424 gr.; N_2=16.7 c.c. (20.5°, 763 mm.) Found: N=13.47%. Calc. for $C_{15}H_{11}O_3N_3 \cdot 2H_2O$: N=13.25%.

1,2-Diphenyl-4-benzylidene-3,5-diketopyrazolidine, [5]. When 2.5 gr. of diphenyl-diketopyrazolidine and 2 gr. of benzaldehyde were heated on the water-bath, the former dissolved into the latter forming a dark red solution, which solidified on cooling to a dark red mass. It was pressed on a porous plate, and washed with alcohol until it smelt no longer of benzaldehyde. The yield was 2.8 gr. The compound has orange red colour, and melts at 164°-165°. It is very soluble in chloroform, moderately soluble in alcohol and ether, but insoluble in ligroin. By the action of hot caustic alkali, it is decolourized and decomposed into its components.

Anal. Subst.=0.1581 gr.; N_2=12.0 c.c. (26°, 764 mm.) Found: N=8.57%. Calc. for $C_{22}H_{16}O_2N_2$: N=8.24%.

1,2-Diphenyl-4-furfurylidene-3,5-diketopyrazolidine, [6]. When 2 gr. of diphenyl-diketopyrazolidine was heated with 1.6 gr. of furfurol on the water-bath for a while, a reddish brown mass was obtained. It was pressed on a porous plate, and washed quickly with alcohol to remove furfurol still adhering to it. The condensation product was left in an almost pure state. The yield was 2 gr. It was once more purified by dissolving it in alcohol and allowing it to stand after the addition of petroleum ether. The compound crystallized out as dark red prisms. It melts at 157°–158°; and is soluble in acetone, benzene and ether. but insoluble in water.

Anal. Subst.=0.1513 gr.; N_2=11.6 c.c. (26°, 763 mm.) Found: N=8.65%. Calc. for $C_{20}H_{14}O_3N_2$: N=8.48%.

1,2-Diphenyl-4-cinnamylidene-3,5-diketopyrazolidine, [7]. 2.5 gr. of diphenyl-diketopyrazolidine and 2.5 gr. of cinnamaldehyde were mixed and heated on a water bath for one hour. The mixture solidified to a dark red mass, which was purified by washing with petroleum ether and alcohol, and dried on a porous plate. The yield was 3 gr. It has a violet-tinged red colour, and is soluble in alcohol, ether and chloroform, sparingly soluble in

ligroin, but insoluble in water. M.p.: 190°–192°. Before melting it seems somewhat to decompose.

Anal. Subst.=0.1490 gr.; N_2=10.2 c.c. (26°, 763 mm.) Found: N=7.72%. Calc. for $C_{24}H_{18}O_2N_2$: N=7.65%.

1,2-Diphenyl-4-[α-phenylethylidene]-3,5-diketopyrazolidine, [9]. Two grams of diphenyl-diketopyrazolidine and 2 gr. of acetophenone were heated for one hour at 130°–180°. On cooling, the product solidified to a reddish brown viscous matter contaminating the yellow needle crystals. It was washed with ligroin, and on recrystallization from alcohol, it gave yellow needles, which melts at 148°–149°. The yield was 0.8 gr. It is soluble in ether and hot alcohol, but insoluble in water.

Anal. Subst.=0.0070 gr.; N_2=0.451 c.c. (23°, 764 mm.) (Pregl's method). Found: N=7.38%. Calc. for $C_{23}H_{18}O_2N_2$: N=7.91%.

1,2-Diphenyl-4-[diphenylmethylene]-3,5-diketopyrazolidine, [10]. Two grams of diphenyl-diketopyrazolidine and 2.8 gr. of benzophenone were fused together on the water-bath for one hour and a half and on a wire gauze, above 100°, for 1/2 hour. The product was extracted with alcohol, and this solution gave reddish yellow needle crystals when allowed to stand for one day. They were recrystallized once from alcohol. M.p.: 265°. The yield was 0.8 gr.

Anal. Subst.=0.0112 gr.; N_2=0.666 c.c. (23°, 758 mm.) (Pregl's method). Found: N=6.75%. Calc. for $C_{28}H_{20}O_2N_2$: N=6.73%.

In conclusion the author wishes to acknowledge his indebtedness to the Department of Education for a grant which has defrayed a part of the expense of this investigation.

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ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART IV.

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Introduction. The oxidation velocity of sodium sulphite, when the mixture of oxygen and air is passed into the solution through a narrow glass-tube under various conditions, and the dissolution velocity of oxygen

into water calculated from the observed value of the oxidation velocity, were reported in the previous papers.[1] In these measurements, the gas bubbles, which ascend in the solution, agitate the solution so violently that in the boundary surface layer a sufficient quantity of sodium sulphite is always present to react with the oxygen molecules which enter into the liquid phase, and the observed oxidation velocity of sodium sulphite gives the dissolution velocity of oxygen into water, when the concentration of sodium sulphite is not below a certain value.

It will be expected that the reaction velocity of the oxidation of sodium sulphite which takes place on the free surface layer of the solution in the atmosphere of oxygen will be independent of the contentration of sodium sulphite and give the dissolution velocity of oxygen into water, when the condition is satisfied under which a sufficient quantity of sodium sulphite is always present in the boundary surface layer.

As will be seen in the subsequent discussion, the dissolution velocity of oxygen, here described, is the value when the concentration of oxygen in the surface layer is maintained at zero.

It is intended in the present paper to report the observed oxidation velocity of sodium sulphite in the atmosphere of oxygen, studied under the following conditions and to give a theoretical consideration on the result.

The direct measurements of the rates of solution of oxygen into water were carried out by several writers.

Adeney and Becker[2] measured the dissolution velocity of oxygen into water from bubbles of known magnitudes. Davis and Crandall[3] carried out the direct measurement of the rates of solution of oxygen into water from the water surface of known area, the main body of water being agitated with a stirrer of special construction.

The initial rate of solution of oxygen into water, observed by these writers, should be equal to the dissolution velocity, calculated from the oxidation velocity of sodium sulphite, if the interpretation above described be acceptable. In Table 4 the values are compared.

Davis and Crandall explained the process of the dissolution velocity of a gas into a liquid by the two film theory,[4] and they assumed the surface of the liquid film is instantaneously saturated with the gas.

The existence of a thin film at the boundary surface may generally be accepted, but it will be difficult to explain the result of the present research

(1) Miyamoto and Kaya, this Bulletin, **5** (1930), 123; Miyamoto, Kaya and Nakata, ibid., **5** (1930), 229; Miyamoto and Kaya, ibid., **5** (1930), 321.
(2) *Phil. Mag.*, **38** (1919), 317; **39** (920), 385; **42** (1921), 87.
(3) *J. Am. Chem. Soc.*, **52** (193), 3757, 3769.
(4) Lewis and Whitman, *Ind. Eng. Chem.*, **16** (1924), 1215.

by the assumption that the surface of the liquid film is instantaneously saturated with the gas, for the oxidation velocity of sodium sulphite is independent of its concentrations. One of the present writers (Miyamoto) has a different opinion on the mechanism of the rate of solution of a gas into a liquid, a part of which is described in the later. The precise discussion on the dissolution theory of a gas will be given in another occasion.

The direct measurement of the rate of solution of oxygen into water was also carried out by Morgan and Pyne,[1] but in their paper the numerical value of the boundary surface area is not given.

Experimental. The apparatus graphically shown in Fig. 1, was employed for the reacting vessel. Oxygen gas, washed by acidified potassium bichromate and sodium hydroxide solutions, is passed at a high velocity through A into the apparatus, which contains 30–50 c.c. of water, for about 30 minutes. When the air in the apparatus has been completely replaced by oxygen, the stirrer S is put in motion at the rate of about 400 revolutions per minute, and a definite quantity of sodium sulphite solution is added in the water from B. The stop-watch is started when about the half volume of the sodium sulphite solution has been poured in the vessel. Oxygen gas is passed at the rate of about 10 liters per hour. The quantity of sodium sulphite added is separately determined by the usual method of iodmetry. The stirrer is made of glass and it is so situated that its wing is vertical to the boundary surface to avoid the disturbance of the surface area.

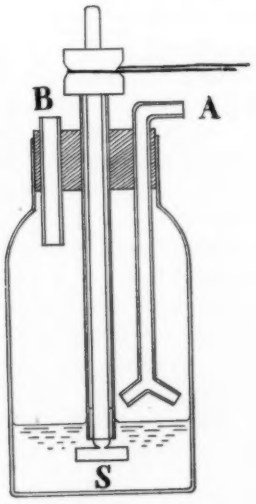

Fig. 1

After the elapse of t- minutes, the oxygen current is stopped and nitrogen gas is passed from B at a high velocity to replace the oxygen in the apparatus quickly. The total quantity of the solution is poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine is titrated back by means of sodium thiosulphate solution.

In Table 1, v is the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the amount of sodium sulphite remained in the vessel. The velocity constant k is calculated by

$$k=\frac{v_0-v}{t},$$

where v_0 is the value of v at $t=0$.

(1) *J. Phys. Chem.*, **34** (1930), 1818.

Table 1.

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c c.	k
15°C.	0.954	17.11	0	148.01	—	—
			50	137.17	137.11	0.217
			0	174.07	—	—
			50	163.05	163.17	0.220
			0	203.71	—	—
			50	193.10	192.81	0.212
			0	230.51	—	—
			50	219.58	219.61	0.219
			0	263.34	—	—
			50	252.30	252.44	0.221
					Mean	0.218
		26.31	0	145.26	—	—
			30	134.54	134.34	0.357
			0	145.41	—	—
			30	134.40	134.49	0.367
			0	179.96	—	—
			30	169.15	169.04	0.360
			0	227.06	—	—
			30	216.13	216.14	0.364
			0	263.06	—	—
			30	251.94	252.14	0.371
					Mean	0.364

Table 1.—(*Continued*)

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c.c.	k
25°C.	0.941	9.22	0	75.24	——	——
			90	54.06	54.45	0.235
			0	93·58	——	——
			90	75.58	72.79	0.225
			0	99.18	——	——
			90	78.58	78.39	0.229
			0	198.11	——	——
			90	177.49	177.32	0.229
			0	220.93	——	——
			96	198.00	198.75	0.239
					Mean	0.231
		17.11	0	134.65	——	——
			50	113.03	112.60	0.432
			0	139.29	——	——
			50	116.00	117.24	0.466
			0	159.77	——	——
			50	137.94	137.72	0.437
			0	185.22	——	——
			50	163.64	163.17	0.432
			0	189.57	——	——
			50	167.76	167.52	0.436
			0	240.14	——	——
			50	218.02	218.09	0.442
					Mean	0.441

Table 1.—(*Continued*)

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c.c.	k
25°C.	0.941	26.31	0	119.67	——	——
			30	98.86	99.21	0.694
			0	121.87	——	——
			30	101.64	101.41	0.674
			0	133.33	——	——
			31	112.05	112.19	0.686
			0	134.67	——	——
			30	114.68	114.21	0.666
			0	140.08	——	——
			30	120.14	119.62	0.665
			0	164.57	——	——
			30	143.88	144.11	0.690
			0	189.52	——	——
			30	168.59	169.06	0.693
			0	209.11	——	——
			30	188.64	188.65	0.682
					Mean	0.682
		42.75	0	122.37	——	——
			20.33	99.83	100.01	1.109
			0	136.47	——	——
			20	113.96	114.47	1.126
			0	163.30	——	——
			50	108.83	108.30	1.089
			0	187.65	——	——
			51.5	130.92	131.00	1.102
			0	209.68	——	——
			50	154.97	154.68	1.094
			0	234.03	——	——
			50	179.86	179.03	1.083
					Mean	1.101

Table 1.—(*Concluded*)

Temp.	p_{O_2} atm.	S cm.^{2}	t min.	v c.c.	$v_{calc.}$ c.c.	k
35°C.	0.916	17.11	0	146.99	—	—
			50	114.88	113.69	0.642
			0	178.43	—	—
			50	146.22	145.13	0.641
			0	205.95	—	—
			50.33	171.15	172.43	0.691
			0	231.99	—	—
			50	198.62	198.69	0.667
			0	261.14	—	—
			50	226.82	227.84	0.686
					Mean	0.666
		26.31	0	147.92	—	—
			30	118.63	117.08	0.976
			0	204.35	—	—
			30.25	173.06	173.25	1.034
			0	235.54	—	—
			30	203.27	204.70	1.076
			0	262.06	—	—
			30	231.50	1.22	1.019
			0	288.99	—	—
			30	257.93	258.15	1.035
					Mean	1.028

The values of $v_{calc.}$ given in the Table, are obtained by

$$v_{calc.}=v_0-kt\,,$$

using the mean value of k.

Under the present conditions, the oxidation velocity is independent of the concentration of sodium sulphite and is proportional to the boundary surface area, as will be seen in Table 1.

The result is easily interpreted by the assumption that the oxidation velocity of sodium sulphite, when it is independent of its concentrations, is not the real reaction velocity but the dissolution velocity of oxygen into water. Then the relation between the observed velocity constant and the dissolution velocity of oxygen is given by

$$D_0=\frac{1}{4}k\times 10^{-4} \text{ moles per minute,} \quad \ldots\ldots\ldots\ldots (1)$$

where D_0 means the dissolution velocity of oxygen into water when its concetration in the surface layer is kept at zero.

The values of $k_{obs.}$ and the dissolution velocity D_0, calculated by the equation (1), are given in the 4th and the 6th column of Table 2.

In the 5th and the 7th column, the values of $k_{calc.}$ and $D_{calc.}$, calculated by the following linear equations with respect to the surface area S, are given.

$$k_{calc.}=0.0133\,S, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$D_{0calc.}=0.332\times 10^{-6}\,S, \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

at 15°C.,

$$k_{calc.}=0.0258\,S, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2')$$

$$D_{0calc.}=0.645\times 10^{-6}\,S, \quad \ldots\ldots\ldots\ldots\ldots\ldots (3')$$

at 25°C. and

$$k_{calc.}=0.0390\,S, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2'')$$

$$D_{0calc.}=0.975\times 10^{-6}\,S, \quad \ldots\ldots\ldots\ldots\ldots\ldots (3'')$$

at 35°C. .

The surface area S is obtained by the measurement of the rise of the level for the addition of a definite volume of water into the vessel.

The partial pressure of oxygen, given in the 2nd column of Table 1 or 2, were calculated from the composition of the gas passed and for the vapour pressure of the solution the vapour pressure of pure water was employed as a first approximation.

Table 2.

Temp.	p_{O_2} atm.	S cm.^{2}	$k_{obs.}$	$k_{calc.}$	$D_{0\,obs.}$ moles/min.	$D_{0\,calc.}$ moles/min.
15°C.	0.954	17.11	0.218	0.228	5.45×10^{-6}	5.70×10^{-6}
		26.31	0.364	0.350	9.10 ,,	8.75 ,,
25°C.	0.941	9.22	0.231	0.233	5.78×10^{-6}	5.95×10^{-6}
		17.11	0.441	0.441	11.03 ,,	11.03 ,,
		26.31	0.682	0.679	17.05 ,,	16.98 ,,
		42.75	1.101	1.103	27.53 ,,	27.58 ,,
35°C.	0.916	17.11	0.666	0.667	16.65×10^{-6}	16.68×10^{-6}
		26.31	1.028	1.026	25.70 ,,	25.65 ,,

The observed result is graphically shown in Fig. 2 and Fig. 3.

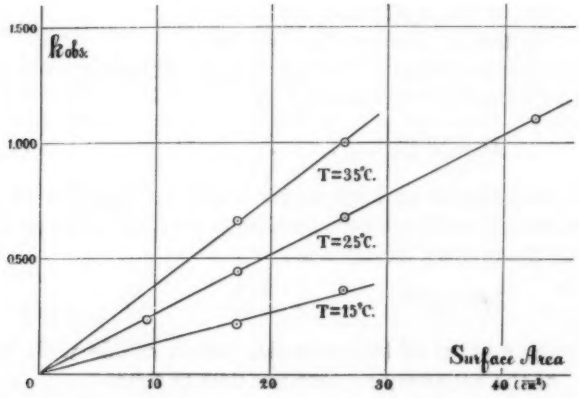

Fig. 2.

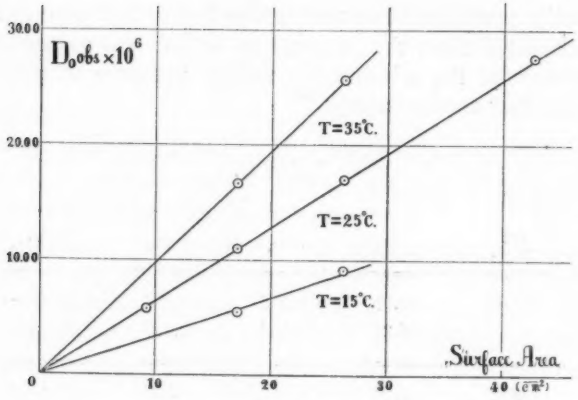

Fig. 3.

Theoretical. The dissolution velocity of a gas into a liquid can generally be given by

$$D=N''S-f(c)S\,, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where N''=the number of the molecules which enter into the liquid phase through the unit boundary surface area per unit of time,

$f(c)$=the number of the molecules which leave the liquid phase through the unit boundary surface area per unit of time, and this value can be considered to be a function of the concentration of the gas in the surface layer,

S=the area of the boundary surface.

When the concentration of the gas in the surface layer is kept at zero, the dissolution velocity is represented by

$$D_0=N''S\,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

This state is maintained so long as the sufficient quantity of a substance which reacts readily with the gas, be always present in the surface layer as in the case of the present experiment.

$$N''=\beta N'\,, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where N'=the number of the molecules which collide with the unit area of the boundary surface per unit of time,

β=the ratio of the number of the molecules which penetrate into the liquid phase and the number of the molecules which collide with the liquid surface.

By Maxwell's distribution law of velocities,

$$dN=\frac{N}{\sqrt{\pi}\,\alpha}e^{-\frac{u^2}{\alpha^2}}du\,, \quad \cdots\cdots\cdots\cdots\cdots\cdots (7)$$

where dN=the number of the molecules whose component of velocity parallel to one axis lies between u and $u+du$ among N molecules.

$$\alpha^2=\frac{2RT}{M}\,, \quad \cdots\cdots\cdots\cdots\cdots\cdots (8)$$

where R=the gas constant,
M=the molecular weight of the gas.

Then,

$$N'=\int_0^\infty \frac{N}{V\sqrt{\pi}\,\alpha}u\,e^{-\frac{u^2}{\alpha^2}}du=\frac{N\alpha}{2V\sqrt{\pi}}\,, \quad \cdots\cdots\cdots\cdots (9)$$

where N=Avogadro's constant,
V=the molar volume.

From (8) and (9),

$$N'=\frac{Np}{\sqrt{2\pi MRT}}\,. \quad \cdots\cdots\cdots\cdots\cdots\cdots (10)$$

Now the following assumption, which has great probability, is adopted. Among the molecules, which collide with the liquid surface, only those molecules, whose components of velocity vertical to the surface are greater than a threshold value u_0, are able to enter into the liquid phase. Then,

$$N''=\int_{u_0}^\infty \frac{N}{V\sqrt{\pi}\,\alpha}u\,e^{-\frac{u^2}{\alpha^2}}du=\frac{N\alpha}{2V\sqrt{\pi}}e^{-\frac{u_0^2}{\alpha^2}}\,, \quad \cdots\cdots (11)$$

or,

$$N''=\frac{Np}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}\,. \quad \cdots\cdots\cdots\cdots\cdots (12)$$

From (6), (10) and (12) we have,

$$\beta=e^{-\frac{Mu_0^2}{2RT}}\,. \quad \cdots\cdots\cdots\cdots\cdots\cdots (13)$$

From (5) and (12),

$$D_0=\frac{Np}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}S \text{ molecules / sec.}$$

$$=\frac{60p}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}S \text{ moles / min.} \quad \cdots\cdots\cdots (14)$$

From (1) and (14),

$$k=\frac{24p\times 10^{-5}}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}S. \quad \cdots\cdots\cdots (15)$$

When all the values except the surface area are kept at constant,

$$D_0=AS, \quad \cdots\cdots\cdots (16)$$

$$k=BS, \quad \cdots\cdots\cdots (17)$$

where A and B are constants.

Thus the experimental equations, above obtained, are theoretically endorsed.

The calculation of the threshold value u_0. From the equations (13) and (15),

$$\beta=\frac{\sqrt{2\pi MRT}}{24p_{o_2}\times 10^5}\frac{k}{S}, \quad \cdots\cdots\cdots (18)$$

$$u_0=\sqrt{\frac{-2RT\ln\beta}{M}}. \quad \cdots\cdots\cdots (19)$$

The value of β, which stands for the ratio of the number of the molecules of oxygen which enter into water and the number of the molecules of oxygen which collide with the liquid surface, can be calculated by the equation (18), using the experimentally obtained values of $\frac{k}{S}$, given in the equations (2), (2′) and (2″).

Then the threshold value u_0 can be calculated by the equation (19).

The values of β and u_0, thus obtained, are given in the 4th and the 5th column of Table 3.

The present calculation is based upon the assumption, that among the molecules of oxygen which collide with the water surface, only the molecule, whose component of velocity is greater than the threshold value u_0, can enter into the liquid phase.

Table 3.

Temp.	p_{O_2} atm.	$\frac{k}{S}$	β	u_0 cm./sec.	$\sqrt{\overline{c^2}}$ cm./sec.
15°C.	0.954	0.0133	1.258×10^{-8}	1.650×10^{5}	4.74×10^{4}
25°C.	0.941	0.0258	2.517×10^{-8}	1.646×10^{5}	4.82×10^{4}
35°C.	0.916	0.0390	3.974×10^{-8}	1.651×10^{5}	4.90×10^{4}

It was first expected that the value u_0 would depend upon the temperature, but the calculated values of u_0 at 15°C., 25°C. and 35°C. are almost identical. It was thus confirmed that the value u_0 is independent of the temperature within the observed region.

The root-mean-square velocity of oxygen molecules, calculated by

$$\sqrt{\overline{c^2}}=\sqrt{\frac{3RT}{M}},$$

is given in the last column of Table 3.

It follows from the present research that only the molecule of oxygen, whose vertical component of velocity is greater than approximately 3.4 times the root-mean-square velocity, can enter into water.

The initial rates of solution of oxygen into water. The initial rates of solution of oxygen into water should be equal to the value D_0, calculated from the maximum oxidation velocity of sodium sulphite, when the water employed is perfectly free from oxygen.

From the equations (3), (3′) and (3″), the dissolution velocity of oxygen from unit surface area per second can be calculated.

Becker[1] measured the absorption velocity of oxygen from air into alkaline water containing suspensions of ferrous hydroxide. It was confirmed that the absorption rate tend to a maximum, independent of further increases in the stirring speed, but the effect of the amount of ferrous hydroxide was not studied. The maximum value should be equal to the initial rates of solution into the alkaline solution. The dissolution velocity of oxygen into alkaline solution is not the same as that into water.[2]

In Table 4 the initial rates of solution of oxygen into water, directly observed, are given in comparison with the values, chemically obtained.

Adeney and Becker observed the initial rates of solution is independent of temperature, while the value, calculated from the oxidation velocity of sodium sulphite by the present writer, depends upon temperature.

(1) *Phil. Mag.*, **45** (1923), 581.
(2) Miyamoto, this Bulletin, **2** (1927), 74; **3** (1928), 98.

Table 4.

Observer	Method	Temp.	Initial rates of solution moles per cm.^{2} per sec.
Davis and Crandall	directly	25°C.	4.5×10^{-9}
,,	,,	25°C.	2.6×10^{-9}
Adeney and Becker	,,	35.1°C.	10.6×10^{-9}
,,	,,	25.2°C.	11×10^{-9}
,,	,,	15.5°C.	11×10^{-9}
,,	,,	2.5°C.	11.3×10^{-9}
Conant and Scherp	,,	25°C.	28×10^{-9}
,,	,,	25°C.	24×10^{-9}
Davis and Crandall	100 c.c. 1N·K_2SO_4 + $Fe(OH)_2$	25°C.	1.0×10^{-9}
Becker	100 c.c. water containing $Fe(OH)_2$ + KOH		5.2×10^{-9}
Miyamoto and Nakata	40 c.c. water containing	15°C.	5.53×10^{-9}
,,	Na_2SO_3 of various	25°C.	11.75×10^{-9}
,,	concentrations	35°C.	16.25×10^{-9}

Summary.

(1) The oxidation velocity of sodium sulphite was studied, when the condition is satisfied, under which the concentration of oxygen in the boundary surface layer is always zero. The oxidation velocity is independent of the concentration of sodium sulphite and is proportional to the boundary surface area.

(2) The theoretical considerations on the observed oxidation velocity was given.

(3) The assumption that only the molecule of oxygen, whose component of velocity vertical to the boundary surface is greater than a threshold value u_0 is able to enter into the liquid phase, was given, and the values of u_0 were calculated at 15°C., 25°C. and 35°C. from the experimentally obtained result.

The calculated value of u_0 is 1.65×10^5 cm. per sec. and is independent of the temperature within the observed region.

The authors wish to express their appreciation of a grant from the Department of Education for the expenses of this research.

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DISPERSOIDAL INVESTIGATIONS ON SELENIUM. I.

By Kiyoshi JUNA.

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Concerning the Influence of the Oxygen and the Carbon Dioxide Present in Air on the Formation of the Dispersed Phase of Selenium when Selenium Solution in Hydrazine Hydrate are poured into Water, Alcohol and Glycerine. Many researches have already been made on the formation of colloidal selenium solutions by pouring into water the selenium solutions in hydrazine hydrate. J. Meyer[1] explained the reaction of the formation of colloidal selenium as follows: ". . . . . Ganz analog wie das Selen verhält sich auch der Schwefel gegen Hydrazine-hydrate,

$$3NH_2NH_3OH + 3S = 2H_2NNH_3SH + H_2NNH_3SO_3H$$
$$6NH_2NH_3OH + 3S = 2(H_2NNH_3)_2S + (H_2NNH_2)_2SO_3 + 3H_2O.$$

. . . . . Beim starken Verdünnen dieser Lösungen erhält man nun kolloide Schwefel- und Selen-Lösung. Die Abscheidung der beiden Elemente ist darauf zurückzuführen, dass die oben gegebenen Reaktionsgleichungen nun von rechts nach links verlaufen . . . . ." A. Gutbier[2] and his collaborator studied also the method of the synthesis of colloidal selenium in aqueous and in alcoholic media.

Experimental. In the following table (this covers only one part of my experiments) are briefly described several experiments showing that the formation of colloidal selenium solutions is dependent principally on the influences of the oxygen and the carbon dioxide present in air.

Conclusion. In an atmosphere of nitrogen any formation of colloidal selenium solution is not to be observed on pouring selenium solutions in hydrazine hydrate into either water, alcohol or glycerine.

I wish to express here to Prof. P. P. von Weimarn my sincere gratitude for providing me with the theme for these investigations.

November 1930. Dispersoidological Department of the Imperial Industrial Research Institute of Osaka.

(1) Meyer, *Ber.*, **46** (1913), 3.
(2) Gutbier, *Ber.*, **47** (1914), 466; *Koll.-Zeitsch.*, **30** (1922), 103.

Table

Medium	In the absence of air; in an atmosphere of nitrogen	Influences of other gases than nitrogen		
		Air	Oxygen	Carbon dioxide
Water	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. H_2O In an atmosphere of nitrogen, no colloidal selenium solutions are formed; but a clear brown solution is obtained.	0.05 c.c. $Se^{2\%}_{H.H.}$ ← 20 c.c. H_2O (In an atmosphere of nitrogen). When air is passed through the clear brown solution obtained, a brick-red colloidal selenium solution is formed.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. H_2O (In an atmosphere of nitrogen). When oxygen is passed through the clear brown solution, a brick-red colloidal solution of selenium is produced.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. H_2O (In an atmosphere of nitrogen). When carbon dioxide is passed through the clear brown solution, a brick-red colloidal selenium solution is formed.
Alcohol	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. C_2H_5OH In an atmosphere of nitrogen, certain selenium compounds do not dissolve readily in alcohol and there results a dark-brown turbid suspension.*	0.3 c.c. $Se^{2\%}_{H.H.}$ ← 20 c.c. C_2H_5OH (In an atmosphere of nitrogen). When air is passed through the above dark-brown turbid suspension, it is transformed into a brick-red colloidal selenium solution, which appears blue in transmitted light.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. C_2H_5OH (In an atmosphere of nitrogen). When oxygen is passed through the above turbid suspension, a brick-red colloidal selenium solution is formed.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. C_2H_5OH (In an atmosphere of nitrogen). When carbon dioxide is passed through the above turbid suspension, a dark-red colloidal selenium solution is obtained, which appears blue in transmitted light.
Glycerine	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. $C_3H_5(OH)_3$ In an atmosphere of nitrogen no colloidal selenium solution is formed; but there results a clear brown solution.	0.3 c.c. $Se^{2\%}_{H.H.}$ ← 20 c.c. $C_3H_5(OH)_3$ (In an atmosphere of nitrogen). When air is passed through the clear brown solution obtained, there is formed a brick-red colloidal solution of selenium.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. $C_3H_5(OH)_3$ (In an atmosphere of nitrogen). When oxygen is passed through the clear brown solution obtained, a brick-red colloidal selenium solution results.	0.2 c.c. $Se^{2\%}_{H.H.}$ ← 40 c.c. $C_3H_5(OH)_3$ (In an atmosphere of nitrogen). When carbon dioxide is passed through the clear brown solution, there is slowly formed a brick-red colloidal selenium solution.

In this table under $Se^{2\%}_{H.H.}$ is designated a 2% selenium solution in hydrazine hydrate.

* By the experiment is shown that the precipitate in the above suspension is decomposed by water containing CO_2 and O_2 from the air. The decomposition is accompanied by the formation of a colloidal selenium solution. After the dissolution of selenium in hydrazine hydrate, the solution was evaporated to dryness under reduced pressure in an atmosphere of nitrogen. To the dry residue obtained, absolute alcohol was added always in the nitrogen atmosphere. After the lapse of a day, the alcohol was filtered off and the residue on a filter paper was washed three times with alcohol, and water, containing CO_2 and O_2 from the air, was added. As a result of the addition of water, the residue suffered decomposition; the dispersed particles of selenium passed through the filter and there was obtained a beautiful, stable colloidal selenium solution of a brick-red colour.

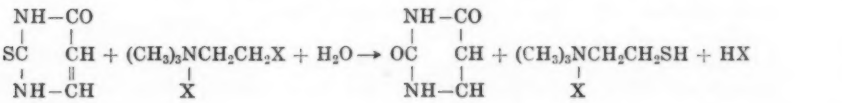
CHEMISTRY OF THIO-CHOLINE HALIDE (TRIMETHYL THIO-ETHYL AMMONIUM HALIDE). II.

NEW THIO-CHOLINE CHLORIDE AND ITS DERIVATIVES.

By Taichi HARADA.

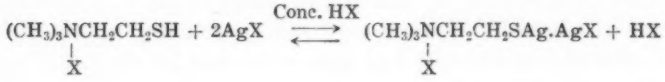
Received December 13, 1930. Published January 28, 1931.

In a previous paper[1] in this Bulletin the author described the preparation of thio-choline bromide and its silver derivatives. The present paper is the continuation of the research on thio-choline compounds. According to the author's previous paper the reaction between 2-thio-uracil and halogeno-choline chloride is represented by the following reaction equation:



The yield was rather small in the pure state owing to side reactions.

Thio-choline chloride forms colorless, transparent monoclinic plates. Above 200°C. thio-choline chloride decomposes slowly. It is interesting to note that the substance forms an addition compound with silver halides giving a complex salt and releasing hydrochloric acid; the reaction becomes decidedly acid. The change may be represented by the following equation:



The new complex compound is a lustrous asbestos-like crystalline salt. The reaction proceeds to the right when the solution is neutral at the start. The compound decomposes slowly into the original constituents under the action of a strong acid or with temperatures above 70°C. It ionizes in aqueous solution probably to form $((CH_3)_3NCH_2CH_2SAg.AgX)^+ + X^-$ ions.

Shortly after the author's first publication, Vickery and Leavenworth[2] reported that cysteine combines with silver sulphate to form a silver compound, $(C_3H_5O_2NS\ Ag)_2Ag_2SO_4$, similar to that of the choline.

Thio-choline halides are very soluble substances both in water and in ethyl alcohol while the silver derivatives are not. The solubility of the

(1) This Bulletin, **4** (1929), 171.

(2) *J. Biol. Chem.*, **83** (1929), 523; **86** (1930), 129.

chlorine compound of the silver derivative, however, is slightly greater in water than that of the corresponding bromide. As a material for the preparation of thio-choline chloride, chloro-choline chloride was prepared by condensation of trimethylamine with ethylene chloride according to the author's previous method for the bromide.[1]

The reaction equation may be represented as follows:

$$(CH_3)_3N + ClCH_2CH_2Cl \longrightarrow (CH_3)_3\underset{\displaystyle Cl}{\overset{|}{N}}CH_2CH_2Cl$$

Chloro-choline chloride decomposes slowly above 163°C. and at 242°C. melts and boils, the color becoming reddish brown. None of these compounds have definite decomposition or melting points.

Experimental Part.

Chloro-Choline Chloride. Forty grams of ethylene chloride were condensed with trimethylamine which was generated from a saturated aqueous solution containing thirty grams of trimethylamine hydrogen chloride in a well-stoppered pressure bottle with a rubber stopper which was framed with an iron cage. It was slowly heated in a water bath, then maintained for several hours at the boiling point of water. With such treatment chloro-choline chloride condensed in the form of a white snow-like salt. The substance obtained was washed with ether and dried over calcium chloride in a desiccator. The yield was forty grams. It can be recrystallized from 95 % ethyl alcohol in a large colorless monoclinic form. It decomposed above 163°C. (approximately), assuming a yellowish tint. At 242°C. (not sharp) it melts and boils changing its color into a reddish brown.

Anal. Subst.=0.2368, 0.1831; AgCl=0.4297, 0.3332 gr. (Carius' method). Found: Cl=44.85, 44.94%. Calc. for $C_5H_{13}NCl_2$: Cl=44.87%.

Thio-Choline Chloride. One molecular proportion (6 gr.) of Chloro-choline chloride was heated with one molecular proportion (5 gr.) of 2-thio uracil together with 25 c.c. of water in a sealed bomb tube at about 150°C. for one to three hours depending upon the size of the tube. After cooling, the sealed tube was opened and transferred to a beaker for the separation of the insoluble uracil formed. The solution was pale yellowish in color. The filtrate was neutralized with a solution of ammonia. The volume of the solution was reduced to a suitable amount on a steam bath. Cooling

(1) This Bulletin, **4** (1929), 171.

permitted further separation of the uracil. The total uracil obtained was 3.91 gr. in the impure state.

Fractional crystallization was then carried out as in the case of thio-choline bromide[1] on the filtrate from the impure uracil. This solution contains ammonium chloride, chloro-choline chloride, and thio-choline chloride. It was treated with butyl alcohol with or without ethyl alcohol and cooled with a mixture of salt and ice. By this repetition a small amount of the transparent colorless monoclinic crystalline form of the substance sought was obtained. The yield in the pure state was about 0.5 gr. It was noticed that some amount of the salt remained in the mother solution.

The compound is a very soluble substance both in water and in ethyl alcohol. Its isoelectric point was found to be at P_H 7.0. Above 200° C. (approximately), it decomposes slowly darkening in color and at 238°C. (not sharp) it melts and boils with a deep brown discoloration.

Anal. Subst.=0.2992; AgCl=0.2744 gr. Found: Cl=22.62%. Calc. for $C_5H_{14}NSCl$: Cl=22.78; S=20.59%.

Subst.=0.2020; AgCl=0.1862; $BaSO_4$=0.3040 gr. (Carius' method). Found: Cl=22.80; S=20.67%.

Silver Derivative of Thio-Choline Chloride. It was found that thio-choline chloride dissolves freshly prepared silver chloride in a slightly acidic or neutral solution giving a pale yellowish solution without any evolution of hydrogen, but with the formation of hydrochloric acid. An excess of freshly prepared silver chloride was dissolved in a solution of thio-choline chloride by constant stirring; the solution becomes a transparent pale yellow. The excess of silver chloride was separated simply by filtration. The filtrate was diluted with 95% alcohol, filtered again, then allowed to stand over-night. From this solution a white lustrous asbestos-like compound was crystallized out. It was separated by filtration, washed with water, alcohol, and ether. Finally it was dried over calcium chloride in a desiccator in the dark,

Second and third crops from the mother solution could be obtained. This was continued until no further separation was evident. The yield is approximately quantitative. It slowly decomposes above 70°C. (approximately); the color changes to gray and then to deep brown; it melts and boils turning dark brown above 228°C. (not sharp). In all probability, this is due mainly to its thermal decomposition products, thio-choline chloride and silver chloride. It ionizes in an aqueous solution, the chlorine-ion precipitating silver chloride from a solution of silver nitrate. The solubility

(1) Ibid, **4** (1929), 174.

of the compound in 100 c.c. of water at 37°C. was found to be 0.1215 gr. while the bromide compound appears to be almost insoluble, that is, 0.0326 gr. under the same conditions.

Hydrogen-ion concentration of the saturated solution of the compound at 37°C. gives P_H 6.9. The structural formula for the compound is still under investigation.

Anal. Subst.=0.1986; AgCl=0.1406 gr. Found: AgCl=70.79%. Calc. for $C_5H_{13}NSAg_2Cl_2$: AgCl=70.63; S=7.90%.

Subst.=0.2400; AgCl=0.1681; $BaSO_4$=0.1398 gr. (Carius' method). Found: AgCl=70.42; S=8.00%.

In concluding, the author withes to express his thanks to Prof. Kraus of Brown University, Prof. Stieglitz of Chicago University, and Dean Whitmore, School of Chemistry and Physics, Pennsylvania State College for valuable private advices regarding the constitution of the silver compound.

Summary.

1. Chloro-choline chloride was obtained by the condensation of trimethylamine with ethylene chloride. It decomposes slowly above 163°C. melting and boiling at 242°C. with a reddish brown discoloration.

2. Thio-choline chloride was prepared from chloro-choline chloride by the action of 2-thio uracil at 150°C. Its isoelectric point was found to be at P_H 7.0. It decomposes slowly above 200°C. (approximately), melting and boiling at 238°C.

3. Thio-choline chloride reacts with silver chloride to form $(CH_3)_3NCH_2CH_2SAg.AgCl$ whose solubility in water at 37° was found to be 0.1215 gr. It decomposes slowly above 70°C. (approximately), melting and boiling around 228°C.

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SOME CONDENSATIONS GIVING DIETHYL DICYANOGLUTACONATE.

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The compound which had been called by the name of diethyl dicyanoglutaconate and to which formula $C_2H_5OCO(CN)C=CH-CH(CN)COOC_2H_5$ or $C_{11}H_{12}O_4N_2$ had been given, was found by the author to be a more complex compound with formula $(C_{11}H_{12}O_4N_2)_2 \cdot H_2O$. The author calls it diethyl dicyanoglutaconate semihydrate, because in this compound half a molecule of water is combined with $C_{11}H_{12}O_4N_2$.[1] Many reactions are known, in which diethyl sodio-dicyanoglutaconate $C_{11}H_{11}O_4N_2Na$ is formed; but treated with a dilute acid, it is transformed, not to the corresponding free cyano-ester $C_{11}H_{12}O_4N_2$, but to the semihydrate $(C_{11}H_{12}O_4N_2)_2 \cdot H_2O$. Hence, the compound with formula $C_{11}H_{12}O_4N_2$, to which the name diethyl dicyanoglutaconate should be given correctly, can not be obtained unless the synthesis is realized without the intermediate formation of the sodium compound. The following condensations were tried, and, in the first two, the formation of diethyl dicyanoglutaconate was ascertained. This compound was not isolated in a pure state, but its presence was proved by the precipitation of diethyl dicyanoglutaconate semihydrate on acidifying the alkali extract of the condensation products, for diethyl dicyanoglutaconate, if present, would dissolve in alkali carbonate forming its own alkali derivative, and the latter, treated with a dilute acid, would give the semihydrate according to the already known process.

(1) *Condensation of ethyl oxymethylene-cyanoacetate* $[HOCH=C(CN)COOC_2H_5]$ *with ethyl cyanoacetate* $[CNCH_2COOC_2H_5]$ *by the action of acetic anhydride.* The reaction was expected to proceed as follows:

$$C_2H_5OCO(CN)C=CHOH + CH_2(CN)COOC_2H_5 = H_2O + C_2H_5OCO(CN)C=CH-CH(CN)COOC_2H_5.$$

A mixture of ethyl oxymethylene-cyanoacetate, ethyl cyanoacetate, and acetic anhydride in molecular proportions was heated for one hour. Then the whole mass was shaken with an aqueous solution of sodium carbonate and ether. On acidifying the aqueous solution, a crystalline substance separated. This was found to be identical with diethyl dicyano-

(1) This Bulletin, **2** (1927), 26.

glutaconate semihydrate, for it melted at 182° and could be transformed into the characteristic picrate melting at 197°.[1]

(2) *Condensation of ethyl chloromethylene-cyanoacetate* [$ClCH=C(CN)COOC_2H_5$] *with ethyl chloro-cyanoacetate* [$ClCH(CN)COOC_2H_5$] *by the action of metallic copper.* Ethyl chloromethylene-cyanoacetate had not been known, but was easily obtained by the action of phosphorus pentachloride on ethyl oxymethylene-cyanoacetate. The mixture of ethyl oxymethylene-cyanoacetate and phosphorus pentachloride in molecular proportions was heated on the water bath. From the reaction product hydrogen chloride and phosphorus oxychloride were removed by heating it on the water-bath and sucking with a water jet pump, and the residue was distilled under diminished pressure. The most part distilled at 106–107° under 16 mm. pressure, and by redistillation the pure substance distilling at 105° under 12 mm. pressure was obtained.

Anal. Found: Cl=22.05, 21.97%. Calc. for $C_6H_6O_2NCl$: Cl=22.23%.

The condensation of ethyl chloromethylene-cyanoacetate and ethyl chlorocyanoacetate was tried at first with so-called molecular silver, but without success. Then metallic copper, which was prepared in fine powder by adding zinc dust to an aqueous solution of copper sulphate, was used. The reaction was too violent, and the whole mass frothed up owing to evolution of an enormous quantity of heat. So in another experiment caution was taken to avoid an excessive rise of temperature. The reaction mass was extracted with ether, and on evaporating the ethereal solution an oily substance was obtained. To examine the presence of diethyl dicyano-glutaconate in this oily substance, it was dissolved in ether, and the ethereal solution was shaken with an aqueous solution of potassium carbonate. A crystalline substance separated from the aqueous solution and proved to be the potassium derivative of diethyl dicyanoglutaconate, for, when its aqueous solution was acidifyed, the yellow crystals of diethyl dicyano-glutaconate semihydrate melting at 182° were obtained, and these gave the characteristic picrate melting at 197°.

The reaction can be represented by the following equation:

$$C_2H_5OCO(CN)C=CHCl + ClCH(CN)COOC_2H_5 + 2Cu \longrightarrow C_2H_5OCO(CN)C=CH-CH(CN)COOC_2H_5 + Cu_2Cl_2$$

(3) *Condensation of ethyl chloromethylene-cyanoacetate* [$ClCH=C(CN)COOC_2H_5$] *with ethyl cyanoacetate* [$CNCH_2COOC_2H_5$] *by the*

(1) This Bulletin, **5** (1930), 7.

action of pyridine. Because of the strong acid nature of ethyl oxymethylene-cyanoacetate it was expected that ethyl chloromethylene-cyanoacetate would act like an acid chloride, and would condense with ethyl cyanoacetate by the action of pyridine, just as acetyl chloride; that is, there must be an analogy between the following reactions:

$$CH_3COCl + CNCH_2COOC_2H_5 + C_5H_5N = C_5H_5NHCl + CH_3CO-CH(CN)COOC_2H_5,$$
$$C_2H_5OCO(CN)C=CHCl + CNCH_2COOC_2H_5 + C_5H_5N = C_5H_5N\cdot HCl + C_2H_5OCO(CN)C=CH-CH(CN)COOC_2H_5.$$

To a mixture of ethyl chloromethylene-cyanoacetate and ethyl cyanoacetate, pyridine was added gradually under cooling. The mixture became a dark red pasty mass. Water and ether were added to the mass, and the two liquids were separated. On acidifying the aqueous solution with dilute sulphuric acid a yellow solid was obtained; but this was found not to be diethyl dicyanoglutaconate semihydrate, but its alcoholic solution gave with picric acid the picrate $C_{11}H_{16}O_6N_2\cdot C_6H_2(NO_2)_3OH$ which is characteristic to diethyl dicyanoglutaconate semihydrate $(C_{11}H_{12}O_4N_2)_2\cdot H_2O$ and to diethyl dicarbamyl-glutaconate $C_{11}H_{16}O_6N_2$. Hence, although the obtained substance were neither of these compounds, it was probably a compound, or a mixture of compounds, which situate between these two in the degree of hydration, and can give the same picrate.

(4) *Condensation of ethyl ethoxymethylene-cyanoacetate* $[C_2H_5OCH=C(CN)COOC_2H_5]$ *with ethyl cyanoacetate* $[CNCH_2COOC_2H_5]$ *by the action of acetic anhydride and zinc chloride.* A mixture of ethyl ethoxymethylene-cyanoacetate, ethyl cyanoacetate, and acetic anhydride in molecular proportions was heated. No change was observed. Zinc chloride was added to the mixture, and boiling was continued for two hours. The mixture became very dark in colour, but no trace of diethyl dicyanoglutaconate was found in the reaction mass.

The author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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(1) Cf. this Bulletin, **2** (1927), 239.